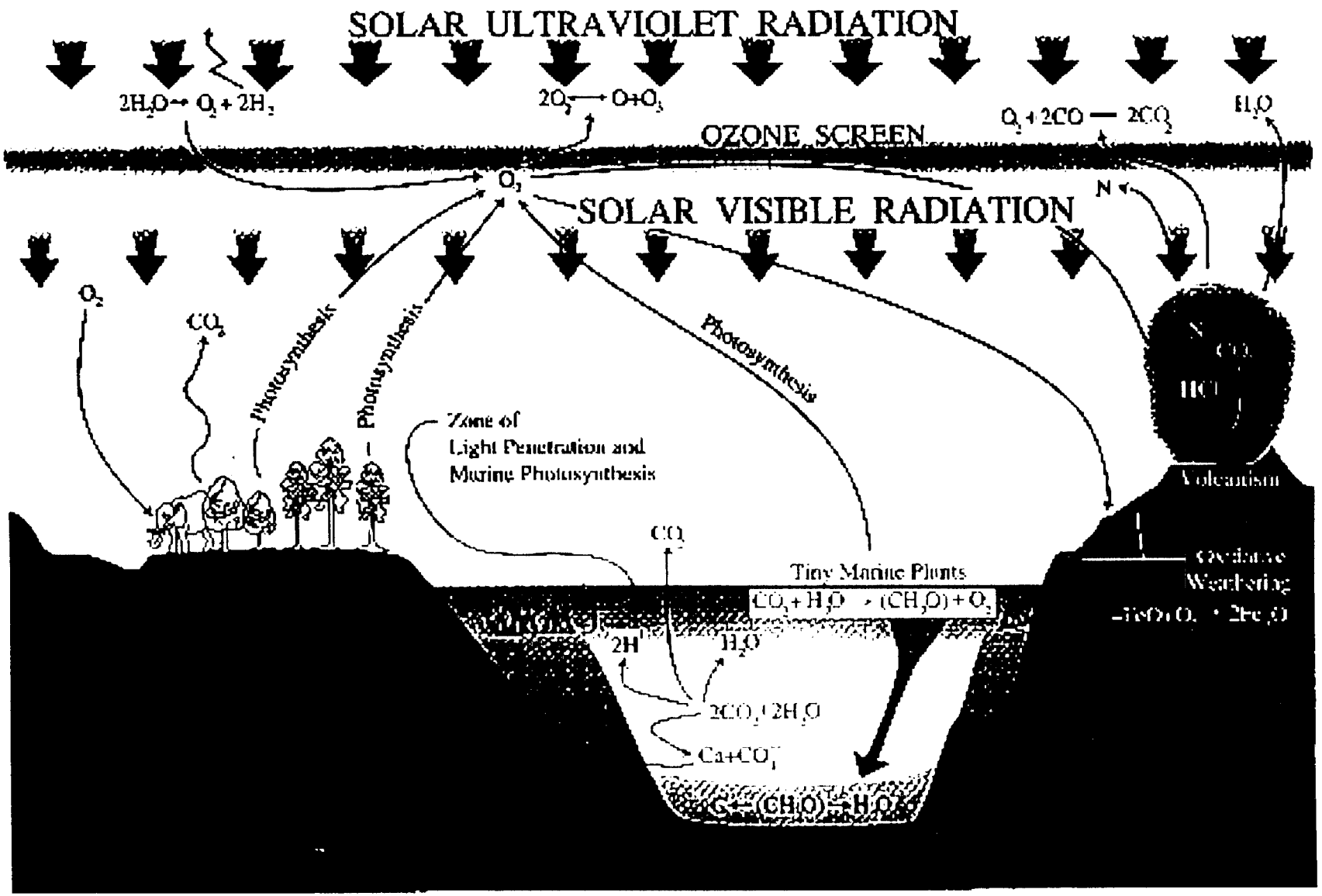
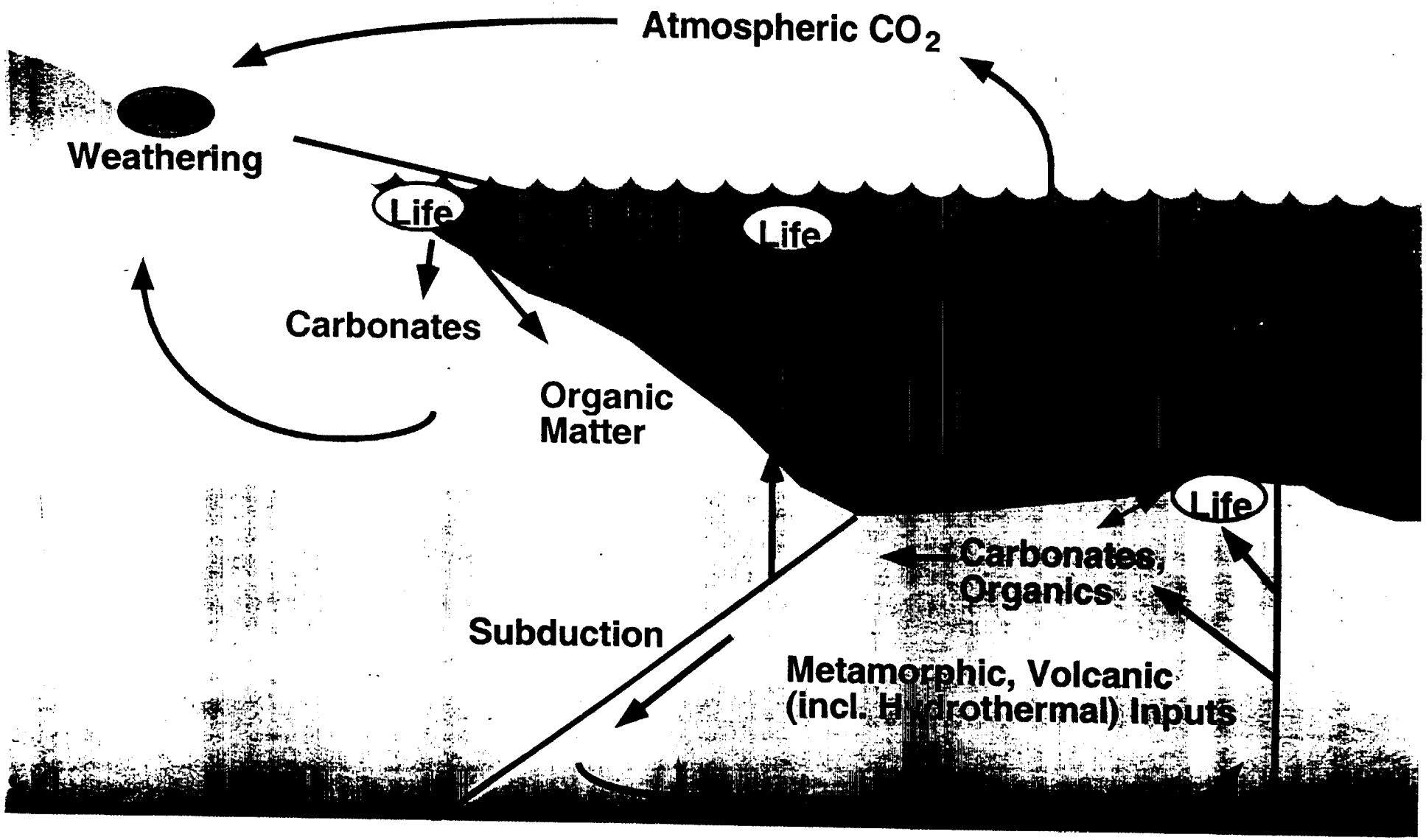


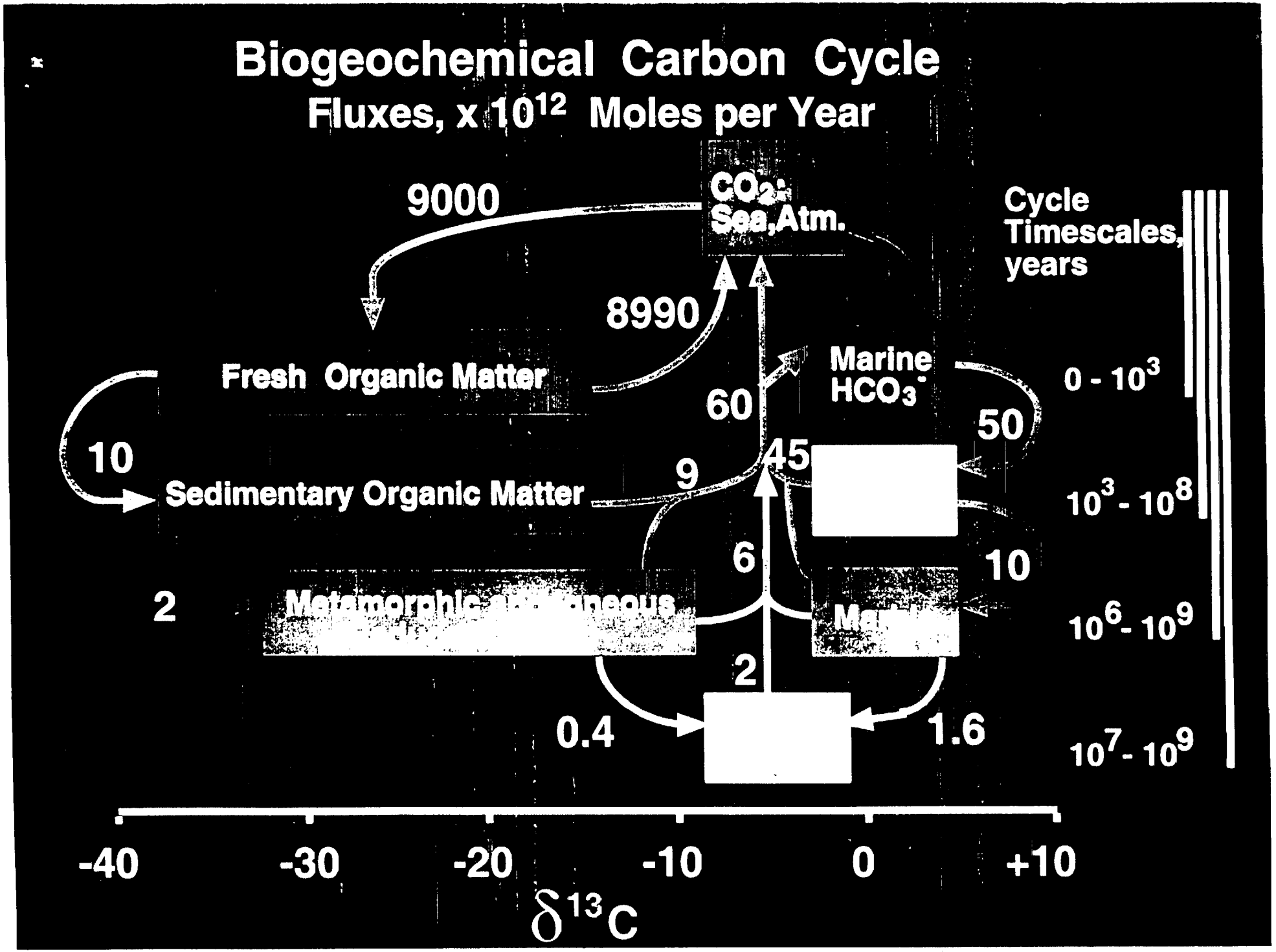
Figure 17.1. Oxygen cycle on Earth today, showing processes that are significant in producing or destroying oxygen. Chemical reactions involving oxygen are summarized; the actual chemistry involves many more steps than the equations on the figure show. Based on Cloud (1988).

Sedimentary Terminal Electron Acceptors
"Bounce per Ounce"

Reaction	Stoichiometry	ΔG° (kJ mol^{-1} of CH_2O)
Oxic Respiration	$CH_2O + O_2 \rightarrow CO_2 + H_2O$	-475
Denitrification	$5CH_2O + 4NO_3^- \rightarrow 2N_2 + 4HCO_3^- + CO_2 + 3H_2O$	-448
Mn-oxide Reduction	$CH_2O + 3CO_2 + H_2O + 2MnO_2 \rightarrow 2Mn^{2+} 4HCO_3^-$	-349
Fe-oxide Reduction	$CH_2O + 7CO_2 + 4Fe(OH)_3 \rightarrow 4Fe^{2+} 8HCO_3^- + 3H_2O$	-114
Sulfate Reduction	$CH_2O + SO_4^{2-} \rightarrow H_2S\ 2HCO_3^-$	-77
Methane Production	$2CH_2O + 2H_2O \rightarrow 2CO_2 + 4H_2$ and $4H_2 + CO_2 \rightarrow CH_4 + 2H_2O$	-58

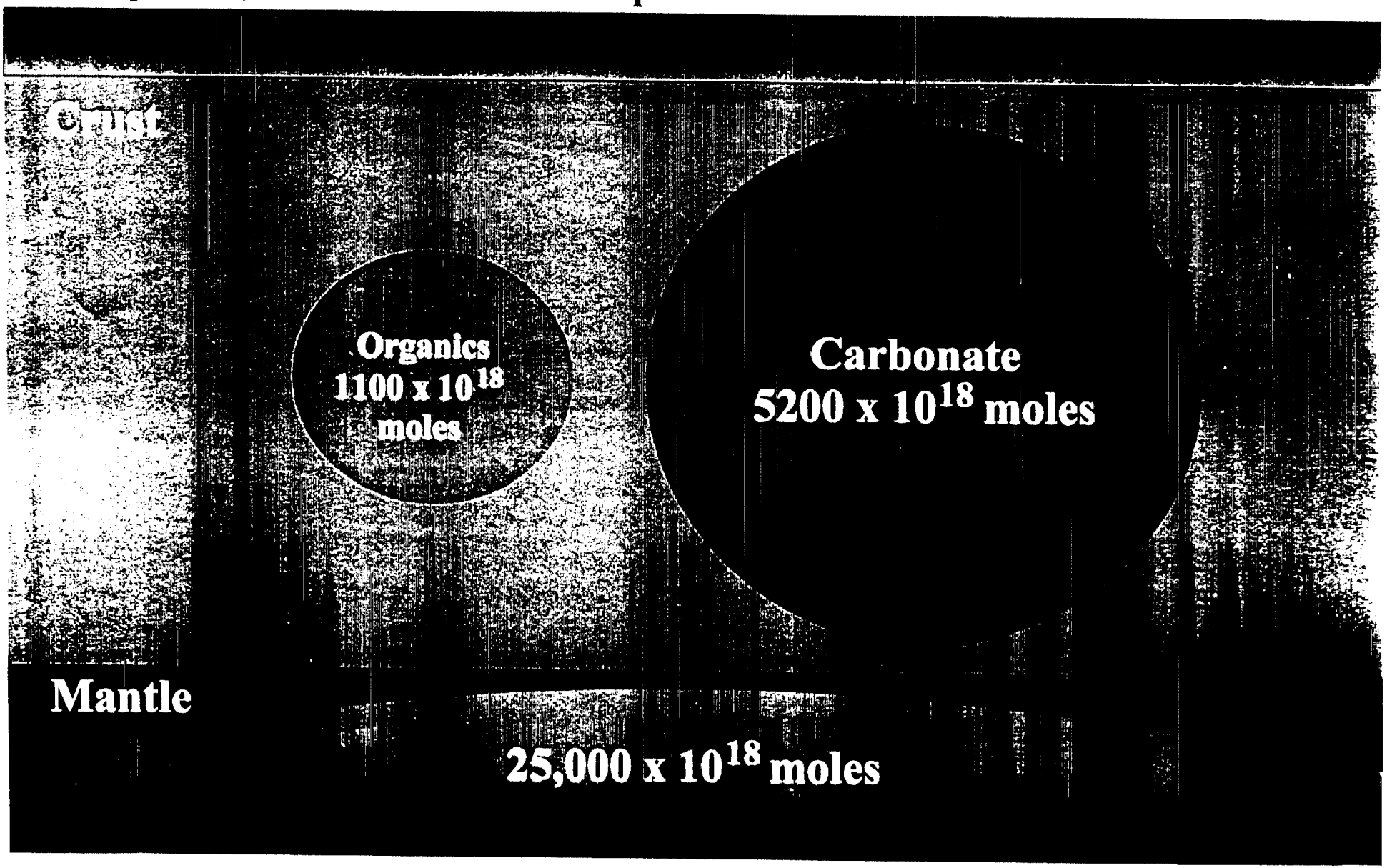
Biogeochemical Carbon Cycle

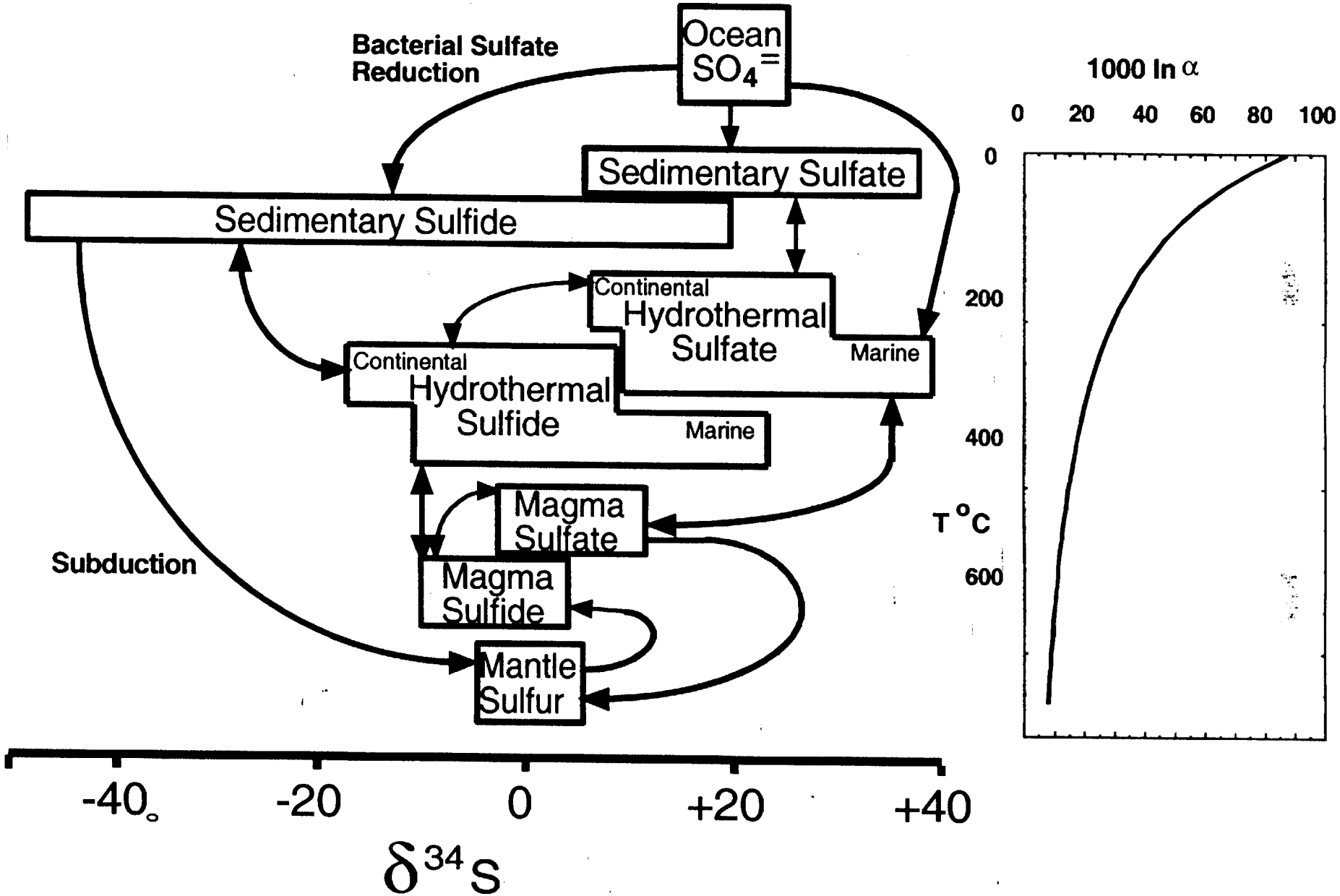



Biogeochemical Carbon Cycle
Fluxes, x 10^12 Moles per Year
9000
CO2: Sea, Atm.
8990
Fresh Organic Matter
Marine HCO3-
60
50
10
45
9
Sedimentary Organic Matter
6
10
2
2
0.4
1.6
-40
-30
-20
-10
0
+10
δ13C
Cycle Timescales, years
0 - 10^3
10^3 - 10^8
10^6 - 10^9
10^7 - 10^9

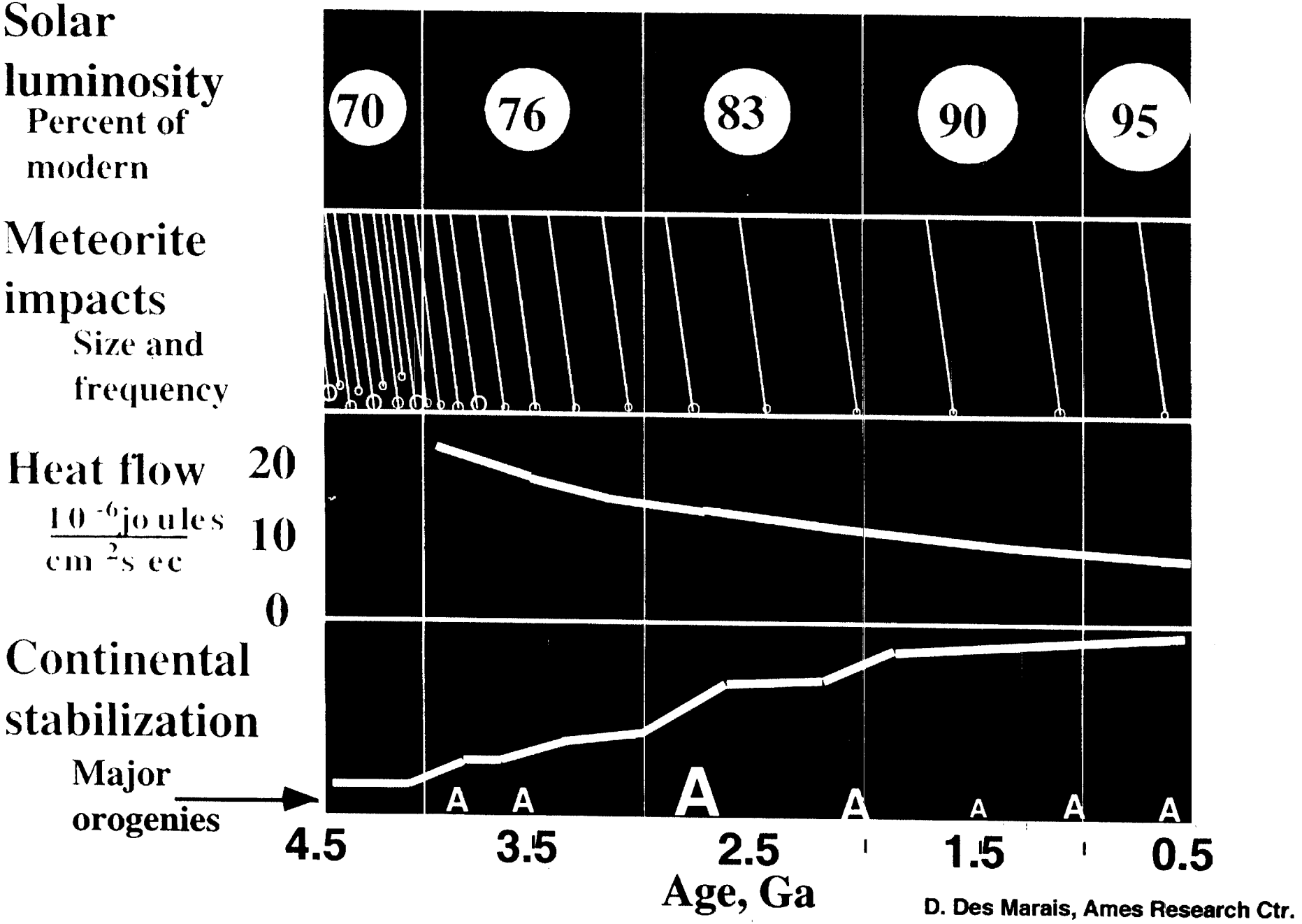
Earth's Carbon Budget

Biosphere, Oceans and Atmosphere • 3.7×10^{18} moles




Bacterial Sulfate Reduction
Ocean $SO_4^=$
Sedimentary Sulfate
Sedimentary Sulfide
Continental Hydrothermal Sulfate
Marine
Continental Hydrothermal Sulfide
Marine
Magma Sulfate
Magma Sulfide
Mantle Sulfur
Subduction
-40‰
-20
0
+20
+40
$\delta^{34}S$
1000 ln α
0
20
40
60
80
100
0
200
400
600
T °C

Evolution of Earth's Early Environment



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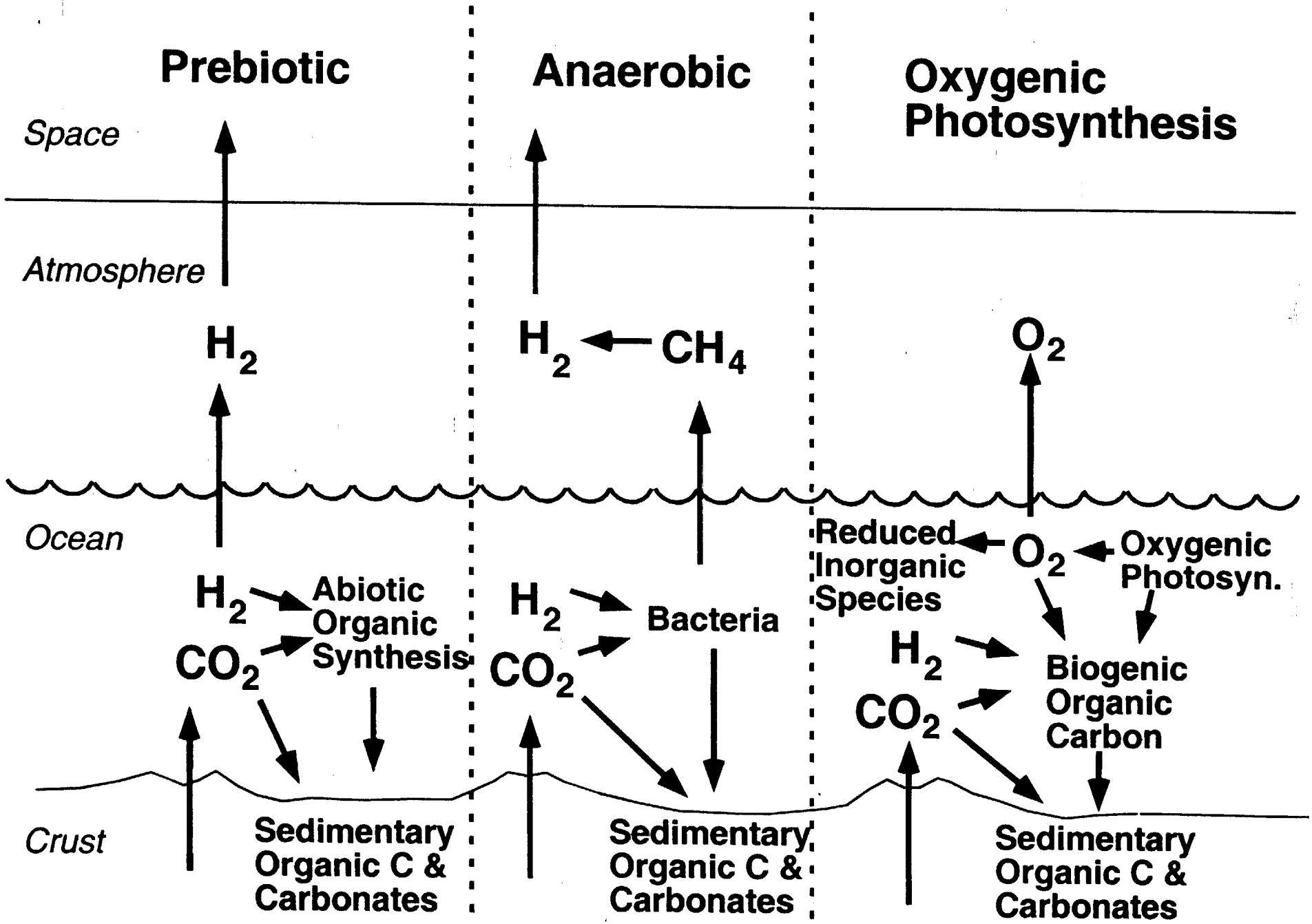
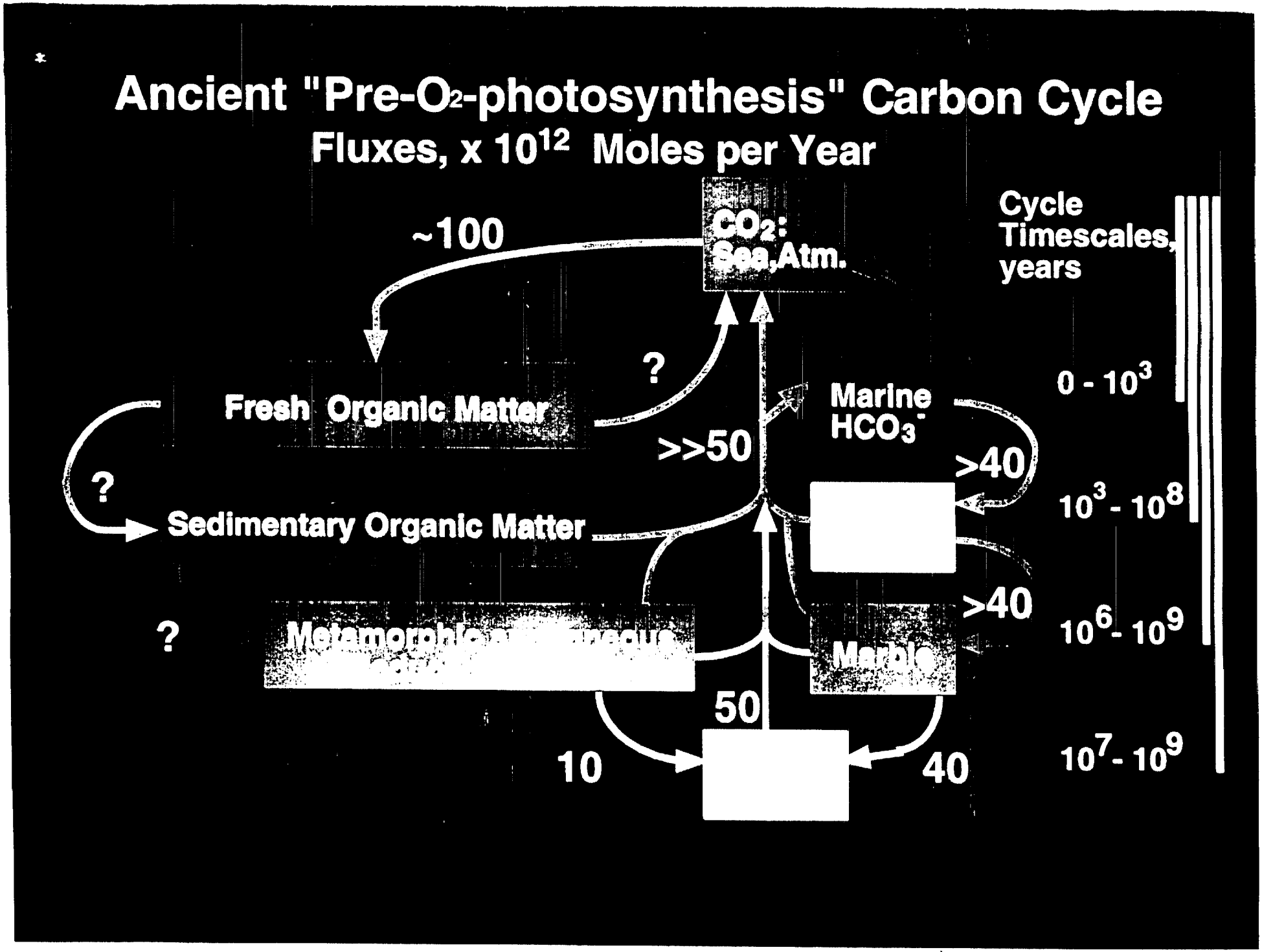
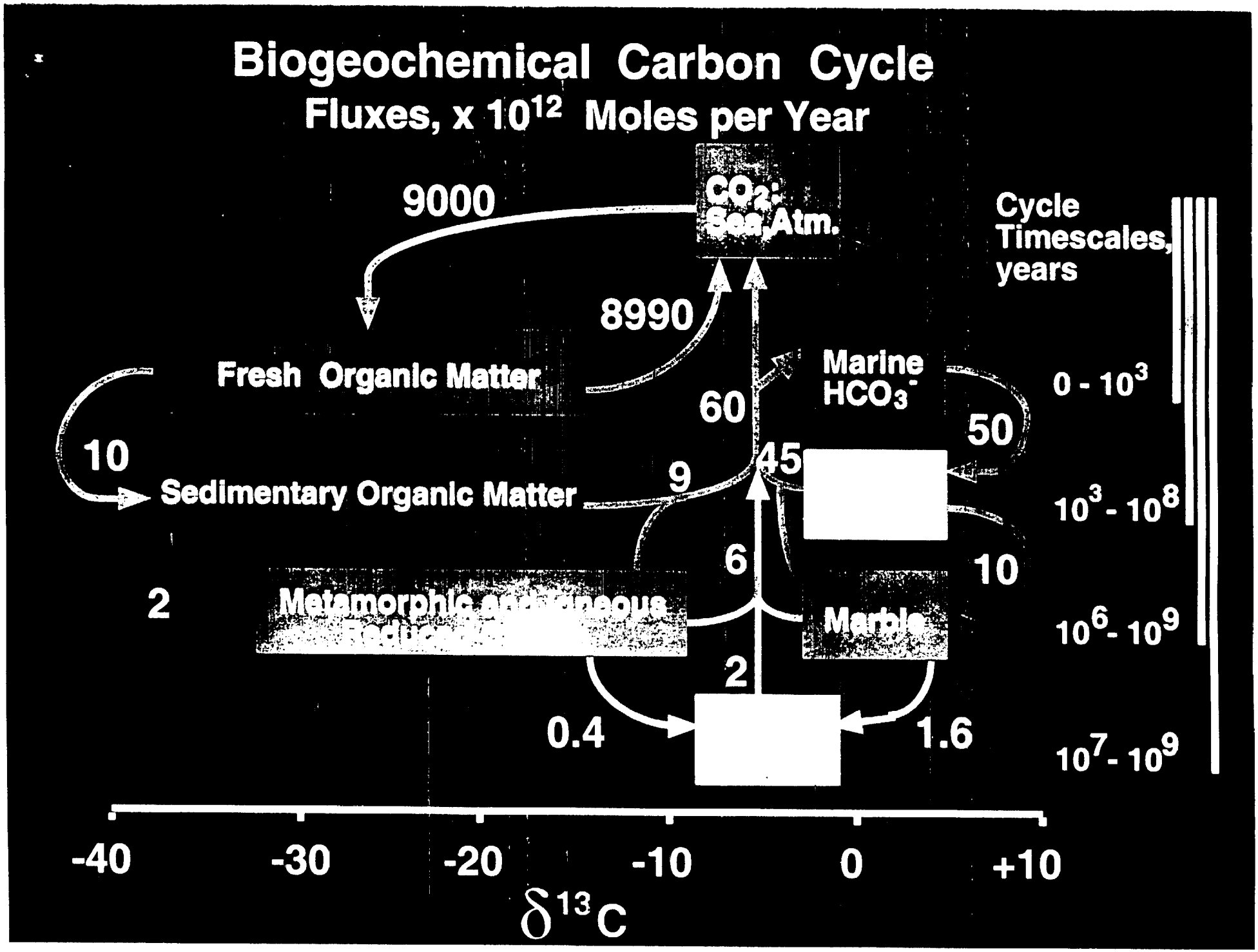

Prebiotic
Anaerobic
Oxygenic Photosynthesis
Space
Atmosphere
H_2
H_2 ← CH_4
O_2
Ocean
Reduced Inorganic Species
O_2
Oxygenic Photosyn.
H_2
CO_2
Abiotic Organic Synthesis
H_2
CO_2
Bacteria
H_2
CO_2
Biogenic Organic Carbon
Crust
Sedimentary Organic C & Carbonates
Sedimentary Organic C & Carbonates
Sedimentary Organic C & Carbonates


Ancient "Pre-O2-photosynthesis" Carbon Cycle
Fluxes, x 10^12 Moles per Year
~100
CO2: Sea, Atm.
Cycle Timescales, years
Fresh Organic Matter
?
Marine HCO3-
0 - 10^3
>>50
>40
?
Sedimentary Organic Matter
10^3 - 10^8
>40
?
Marble
10^6 - 10^9
50
10
40
10^7 - 10^9

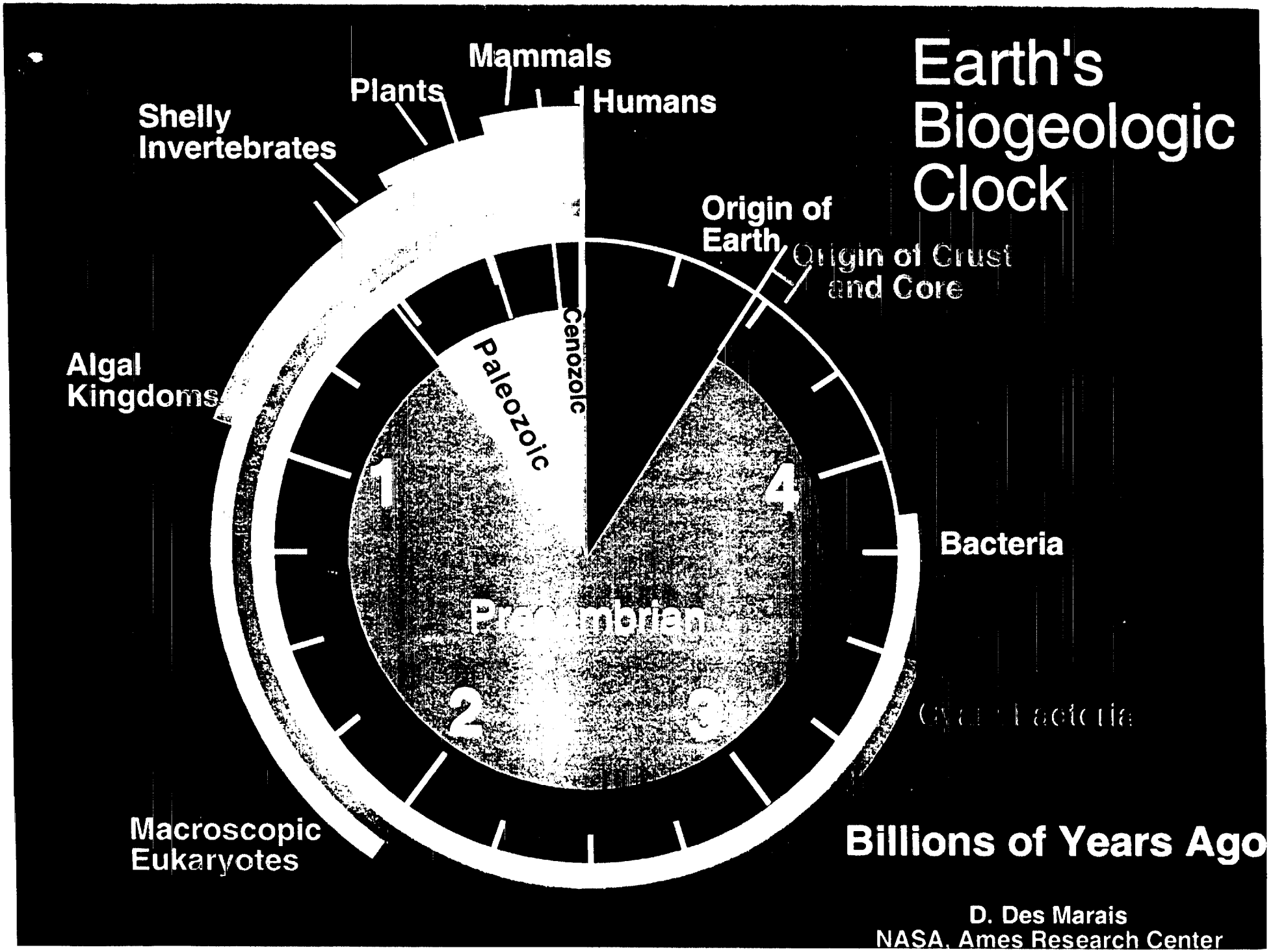

Biogeochemical Carbon Cycle
Fluxes, x 10^12 Moles per Year
9000
CO2: Sea, Atm.
8990
Fresh Organic Matter
Marine HCO3-
60
50
10
45
9
Sedimentary Organic Matter
6
10
2
Metamorphic
Marble
2
0.4
1.6
Cycle Timescales, years
0 - 10^3
10^3 - 10^8
10^6 - 10^9
10^7 - 10^9
-40
-30
-20
-10
0
+10
δ13C

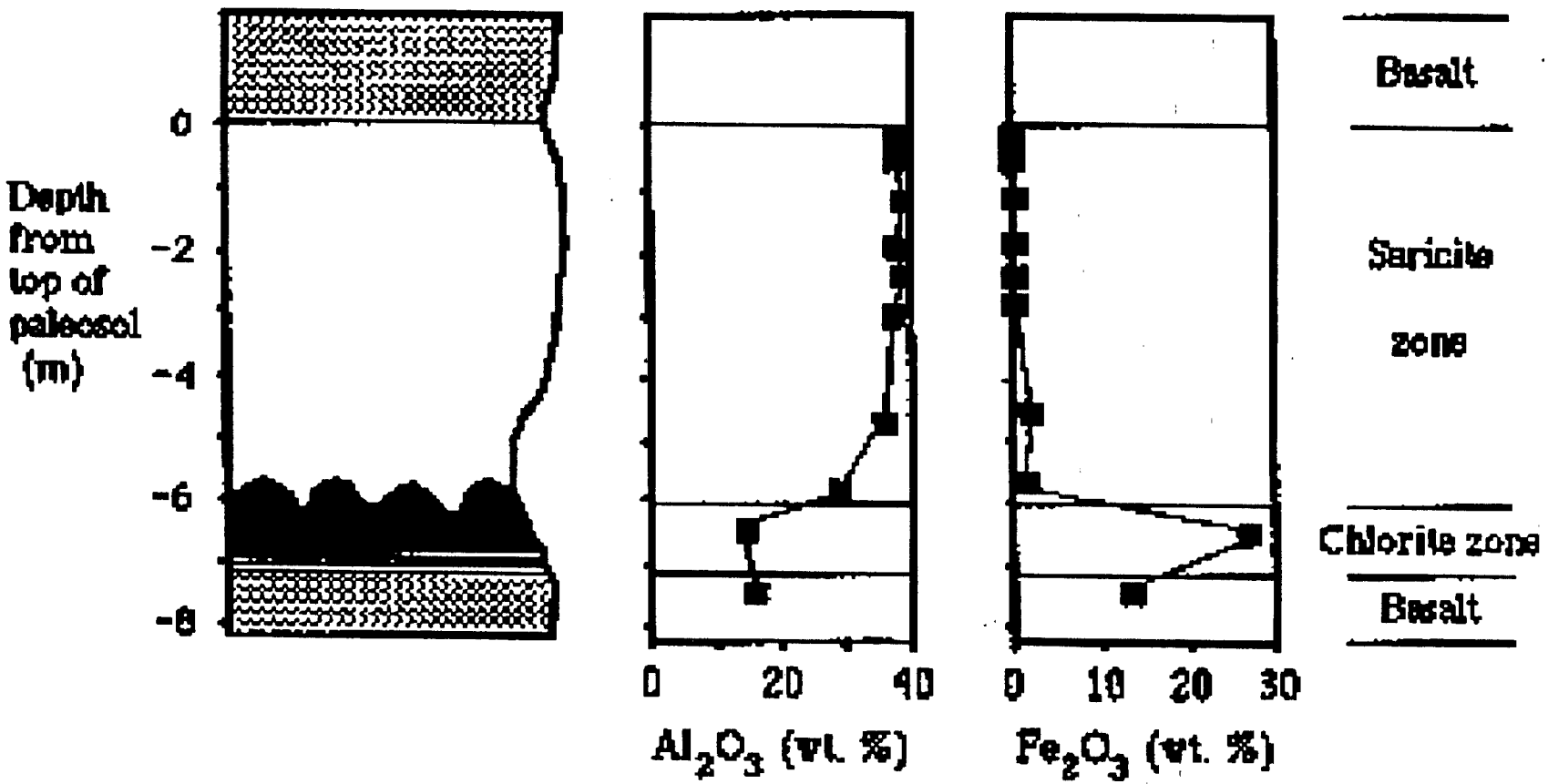
Oxygenic photosynthesis in the Archean (Part 1)

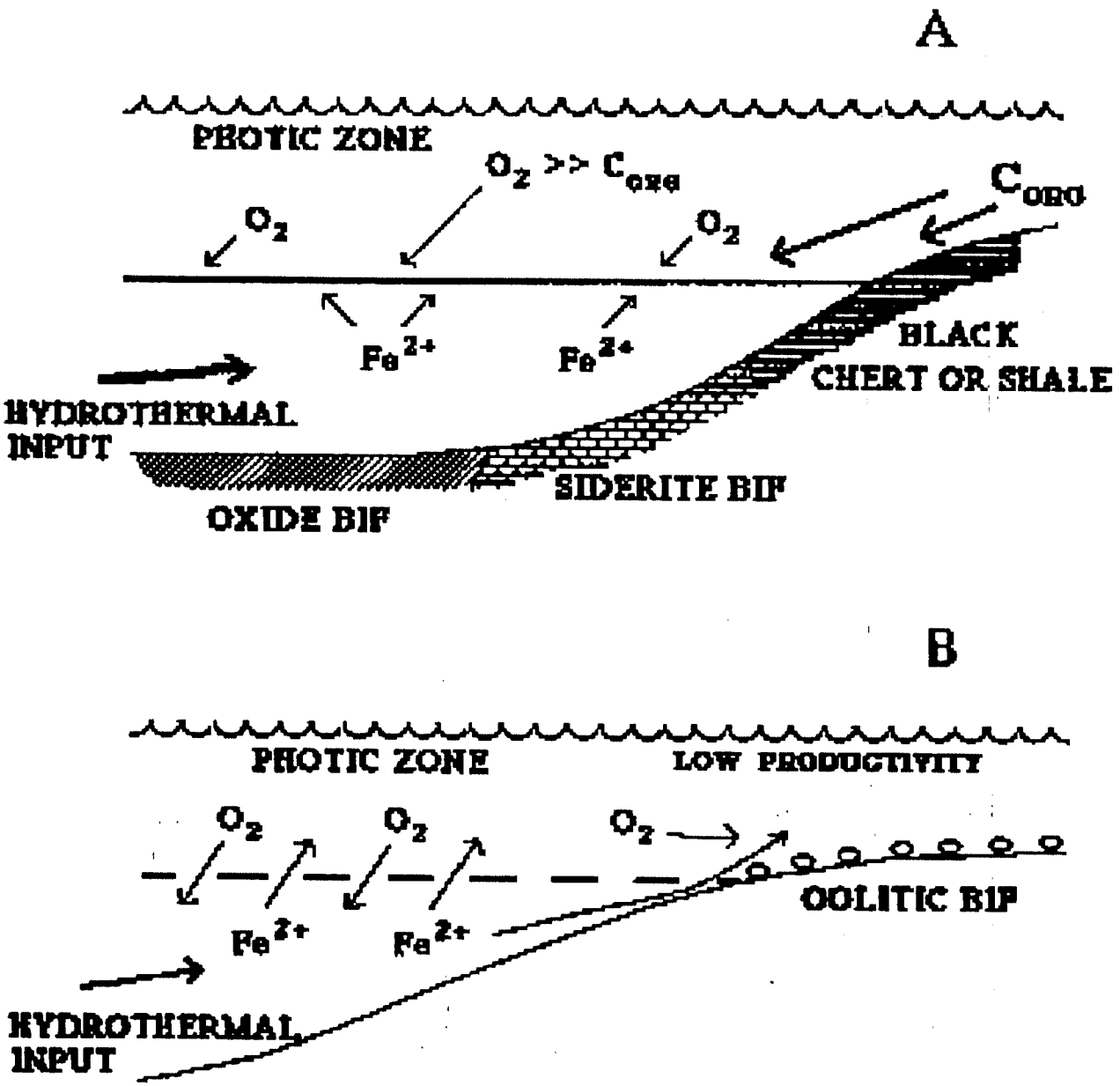
- Microfossils strongly resembling cyanobacteria: segmented filaments, coccoid clusters & sheaths having "correct" dimensions (Apex: 3.4 Ga, Fortescue: 2.7 Ga)
- Stromatolites & biofilms in lakes and shallow marine environments (not near thermal vents, etc.) consistent with O_2 photosynthetic communities (Fig Tree? & Warrawoona?: 3.4^{+} Ga; Pongola: 3.0 Ga, Fortescue: 2.7 Ga)
- Isotopically very light kerogens and normal carbonates consistent with a consortium of CO_2 autotrophs-methanogens-methanotrophs (Fortescue & Ventersdorp: 2.7 Ga)

Oxygenic photosynthesis in the Archean (Part 2)

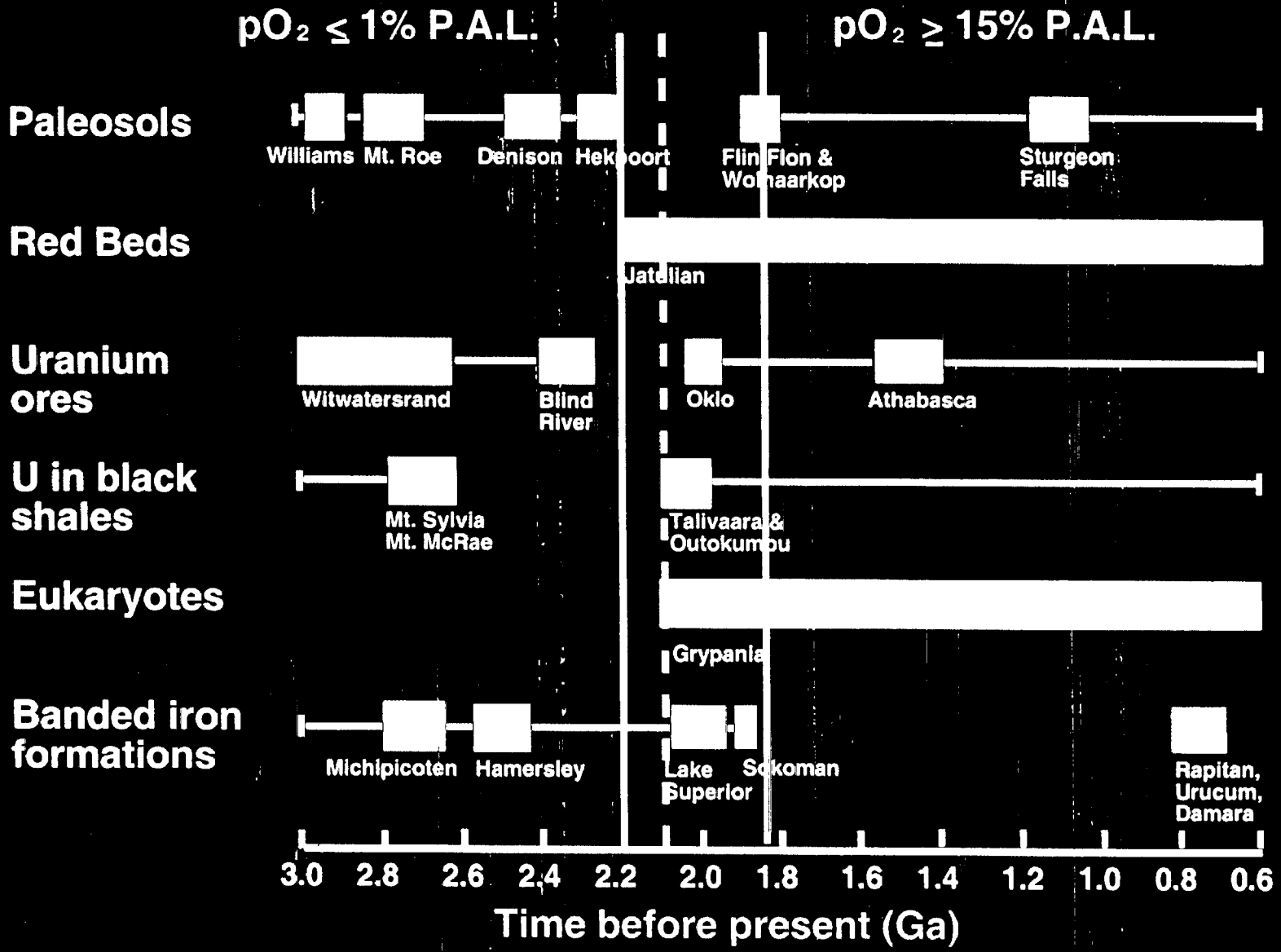
- Robust carbonate platform & reef formation closely analogous to modern examples: high-productivity communities (Transvaal: 2.5 Ga and younger)
- Oxidation of Fe^{2+} to Fe^{3+} in outer marine platform margins below the photic zone, with net deposition of Fe^{3+} (i.e., little or no local bio-organosynthesis)
- Organic concentrations in Archean cherts, carbonates and shales very similar to organic concentrations in Proterozoic and Phanerozoic lithologies
- Geochemical evidence for SRB at 2.7 Ga (McRae Sh), together with rRNA evidence for simultaneous divergence of SRB and cyanobacterial lineages

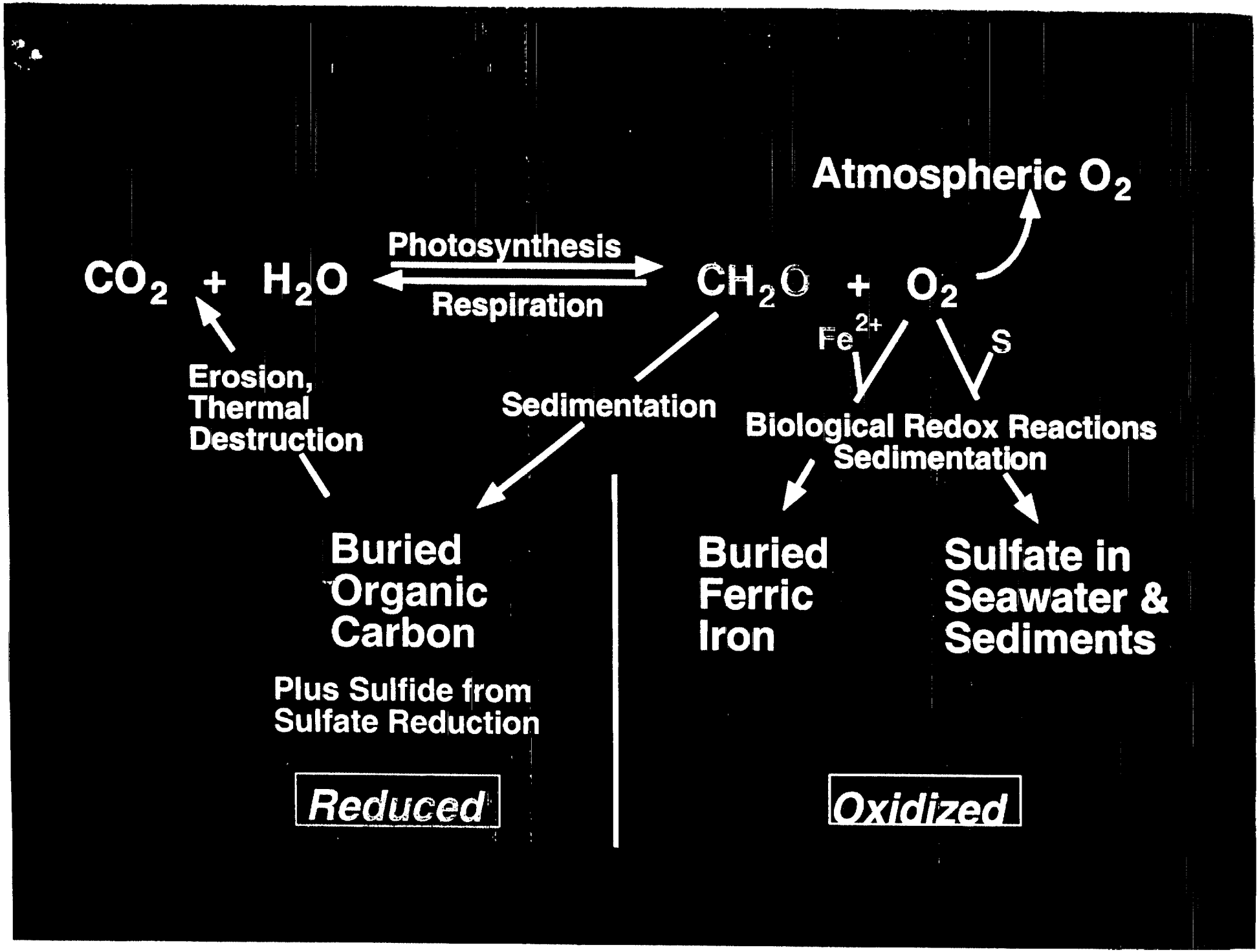

Earth's Biogeologic Clock
Mammals
Plants
Humans
Shelly Invertebrates
Origin of Earth
Origin of Crust and Core
Cenozoic
Paleozoic
Algal Kingdoms
Bacteria
Macroscopic Eukaryotes
Billions of Years Ago
D. Des Marais
NASA, Ames Research Center

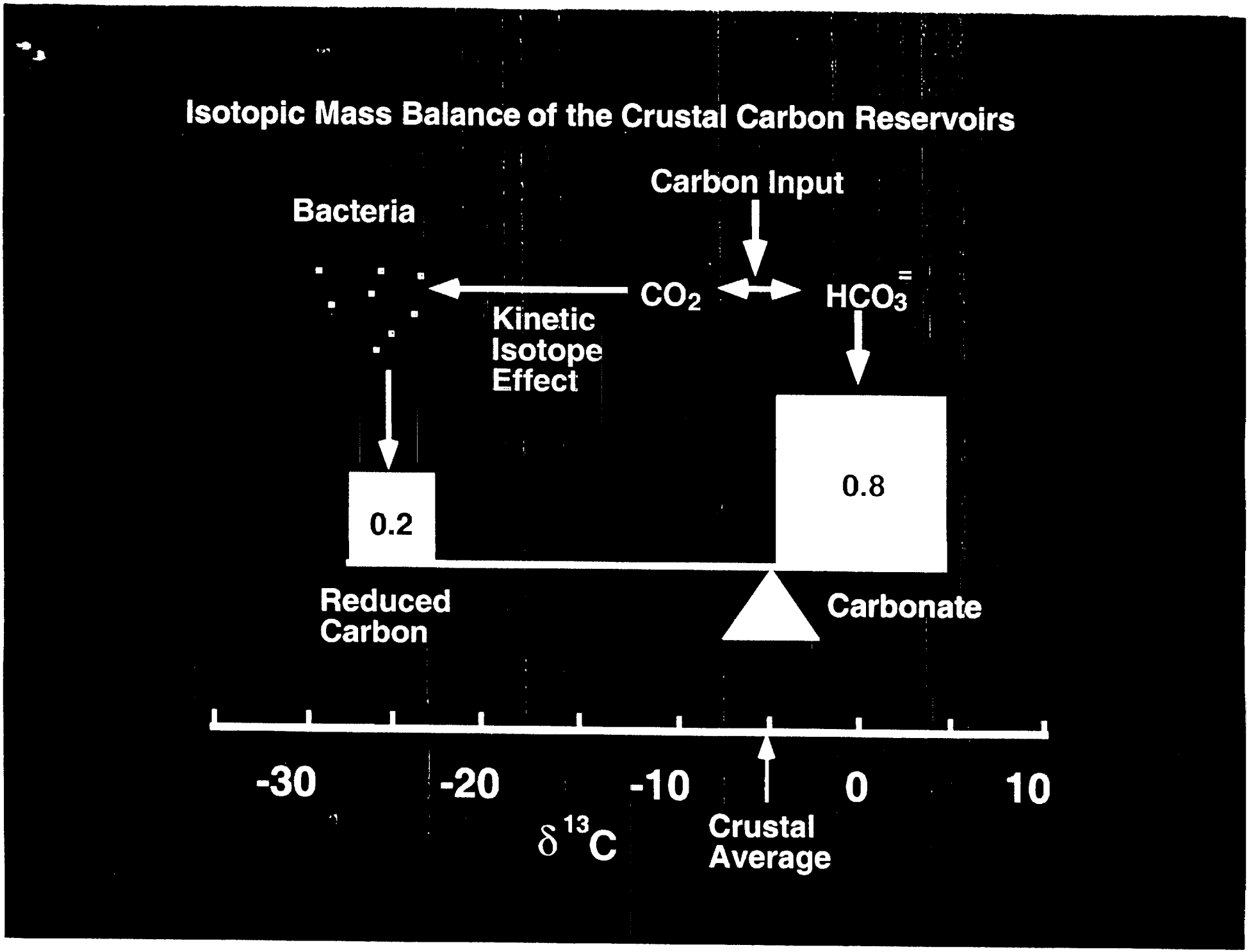

Depth from top of paleosol (m)
0
-2
-4
-6
-8
0
20
40
Al_2O_3 (wt. %)
0
10
20
30
Fe_2O_3 (wt. %)
Basalt
Sericite zone
Chlorite zone
Basalt


A
PHOTIC ZONE
$O_2 >> C_{org}$
C_{ORG}
O_2
O_2
Fe^{2+}
Fe^{2+}
BLACK
CHERT OR SHALE
HYDROTHERMAL
INPUT
SIDERITE BIF
OXIDE BIF
B
PHOTIC ZONE
LOW PRODUCTIVITY
O_2
O_2
O_2
OOLITIC BIF
Fe^{2+}
Fe^{2+}
HYDROTHERMAL
INPUT

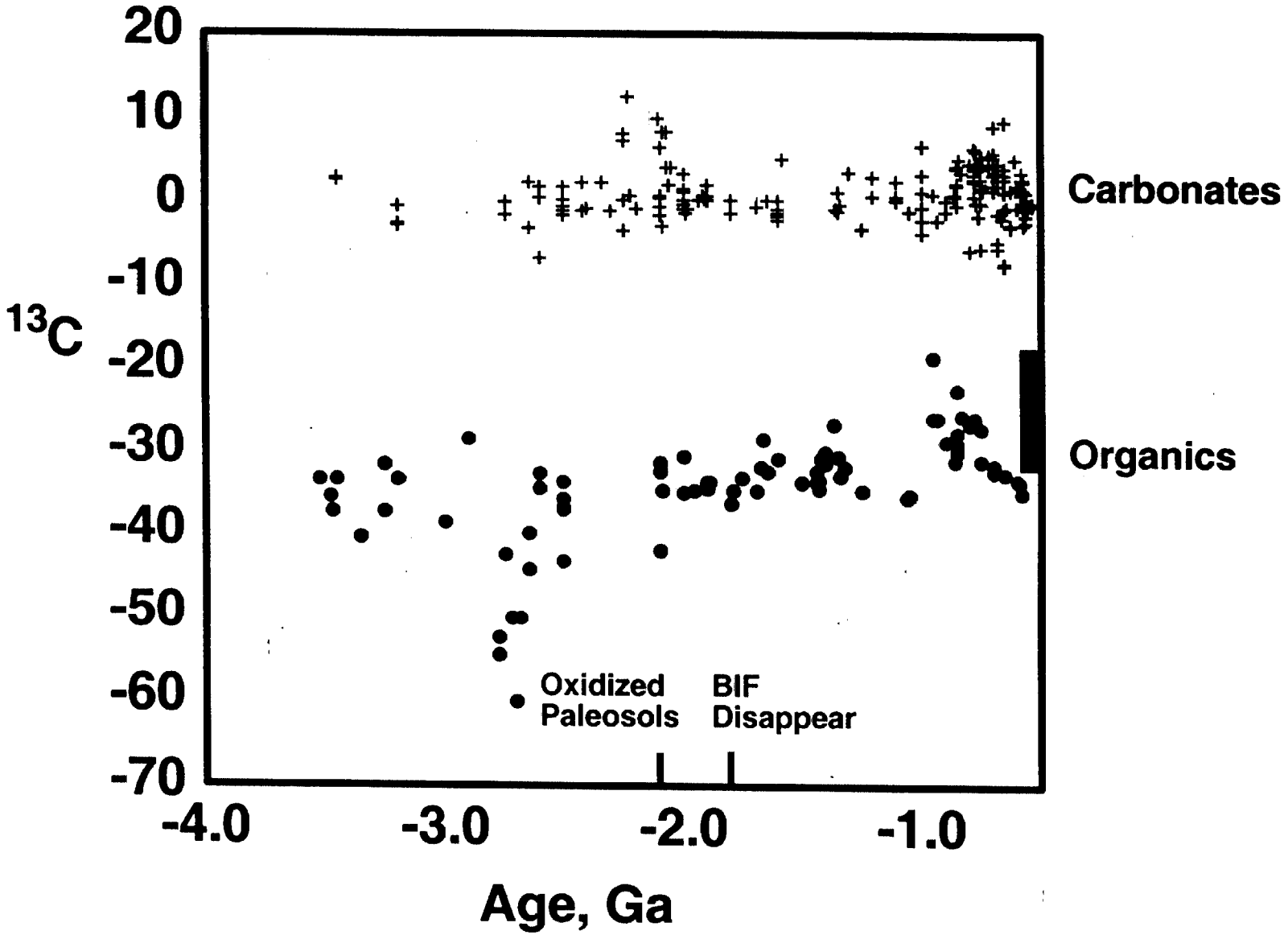
Evidence for the Oxidation of Earth's Environment

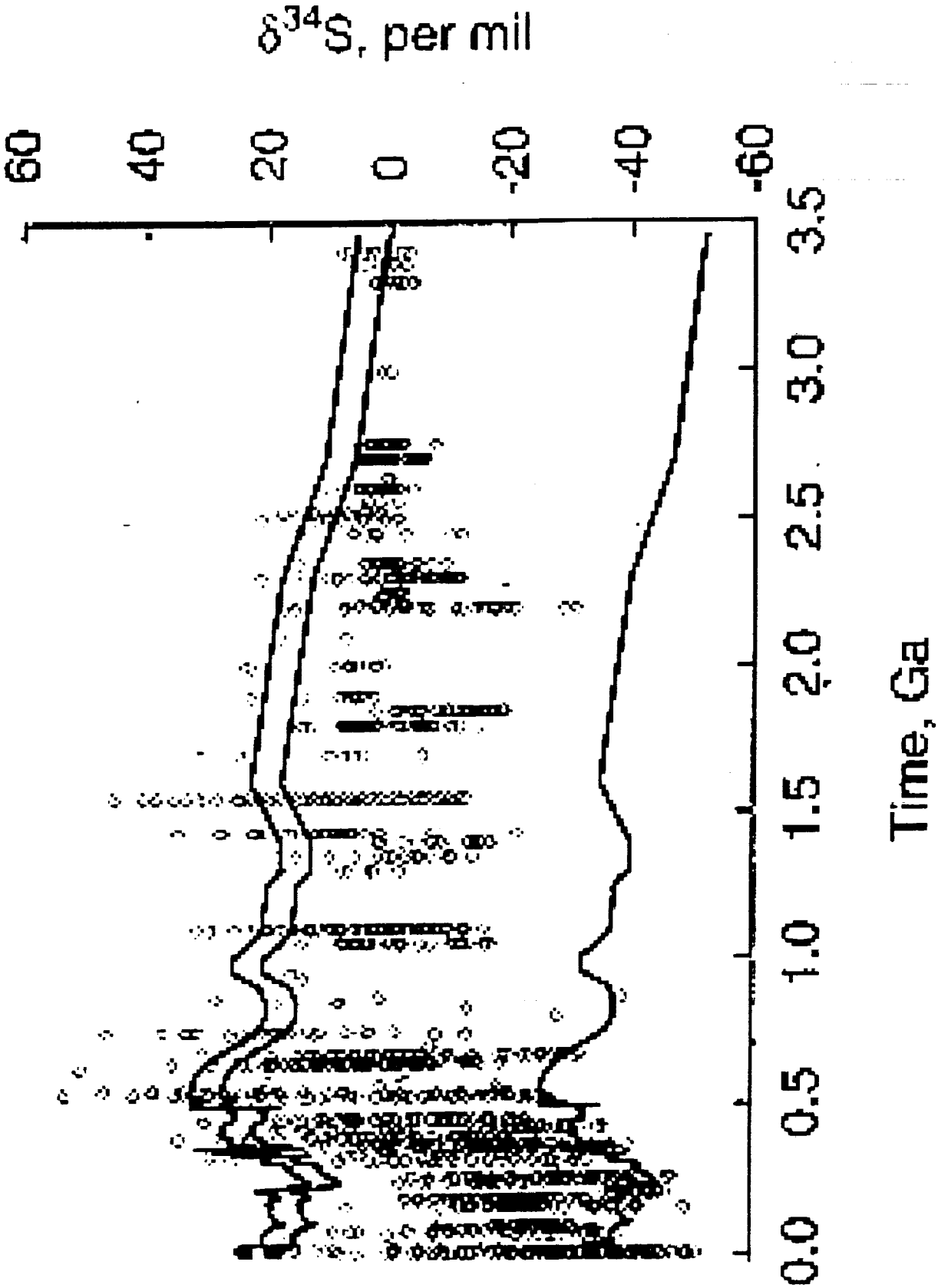


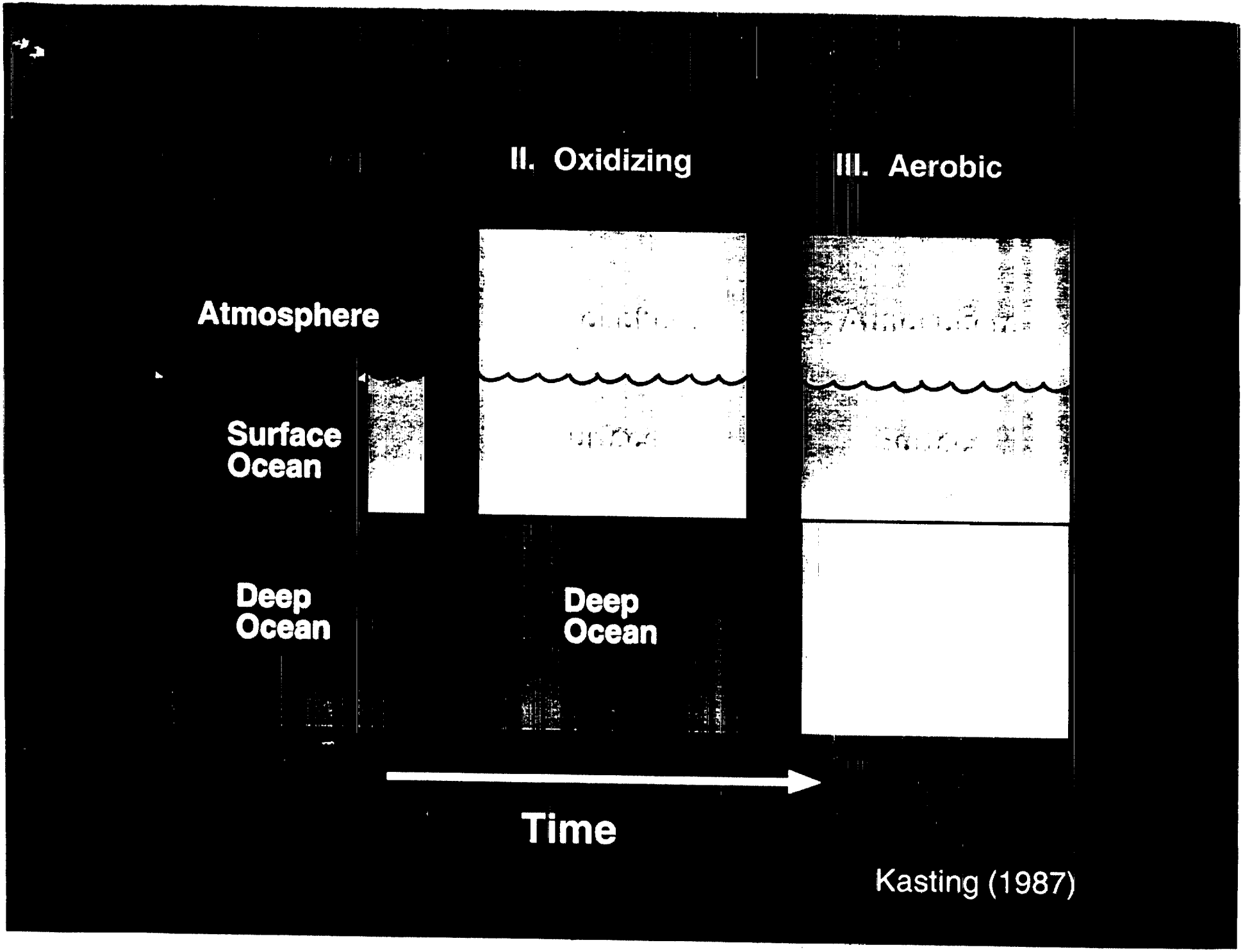

Atmospheric O_2
CO_2 + H_2O
Photosynthesis
Respiration
CH_2O + O_2
Fe^{2+}
S
Erosion,
Thermal
Destruction
Sedimentation
Biological Redox Reactions
Sedimentation
Buried
Organic
Carbon
Plus Sulfide from
Sulfate Reduction
Buried
Ferric
Iron
Sulfate in
Seawater &
Sediments
Reduced
Oxidized


Isotopic Mass Balance of the Crustal Carbon Reservoirs
Carbon Input
Bacteria
CO_2
$HCO_3^=$
Kinetic
Isotope
Effect
0.2
0.8
Reduced
Carbon
Carbonate
-30
-20
-10
0
10
$\delta^{13}C$
Crustal
Average

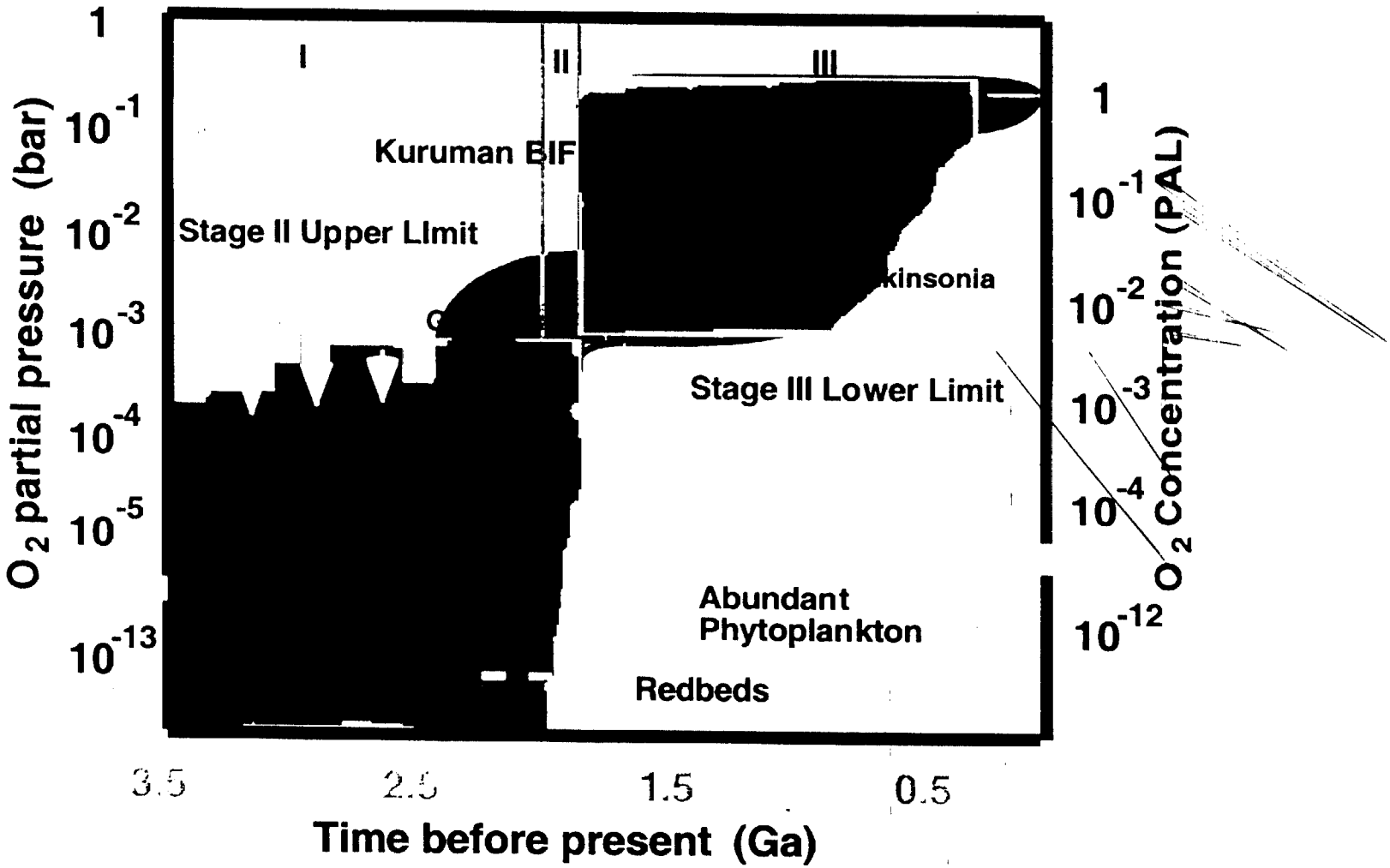
Carbon Isotopic Record in Sedimentary Carbonates and Organic Matter




δ34S, per mil
60
40
20
0
-20
-40
-60
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
Time, Ga

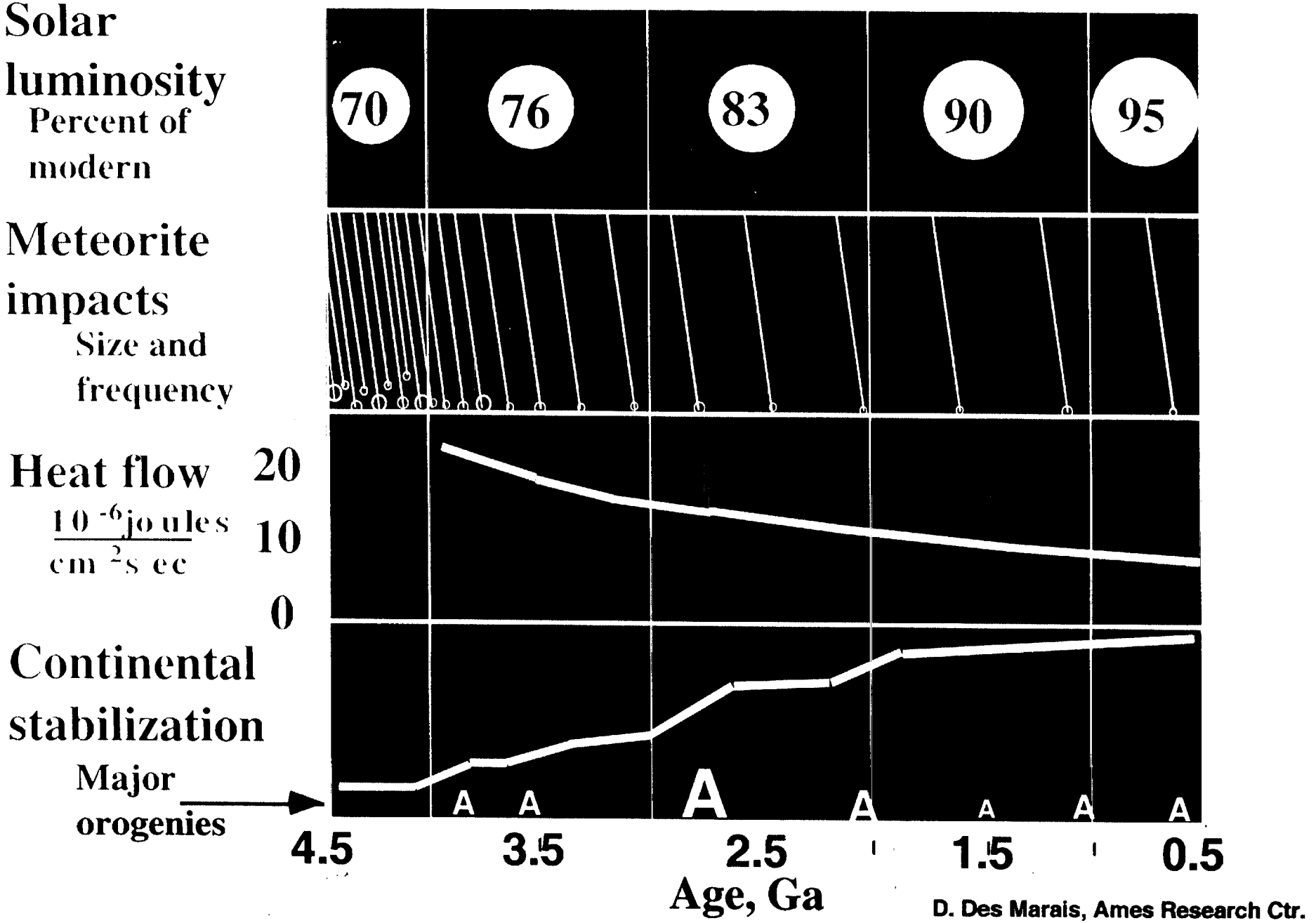

II. Oxidizing
III. Aerobic
Atmosphere
Surface Ocean
Deep Ocean
Deep Ocean
Time
Kasting (1987)

Rise of Atmospheric Oxygen



J. Kasting

Evolution of Earth's Early Environment



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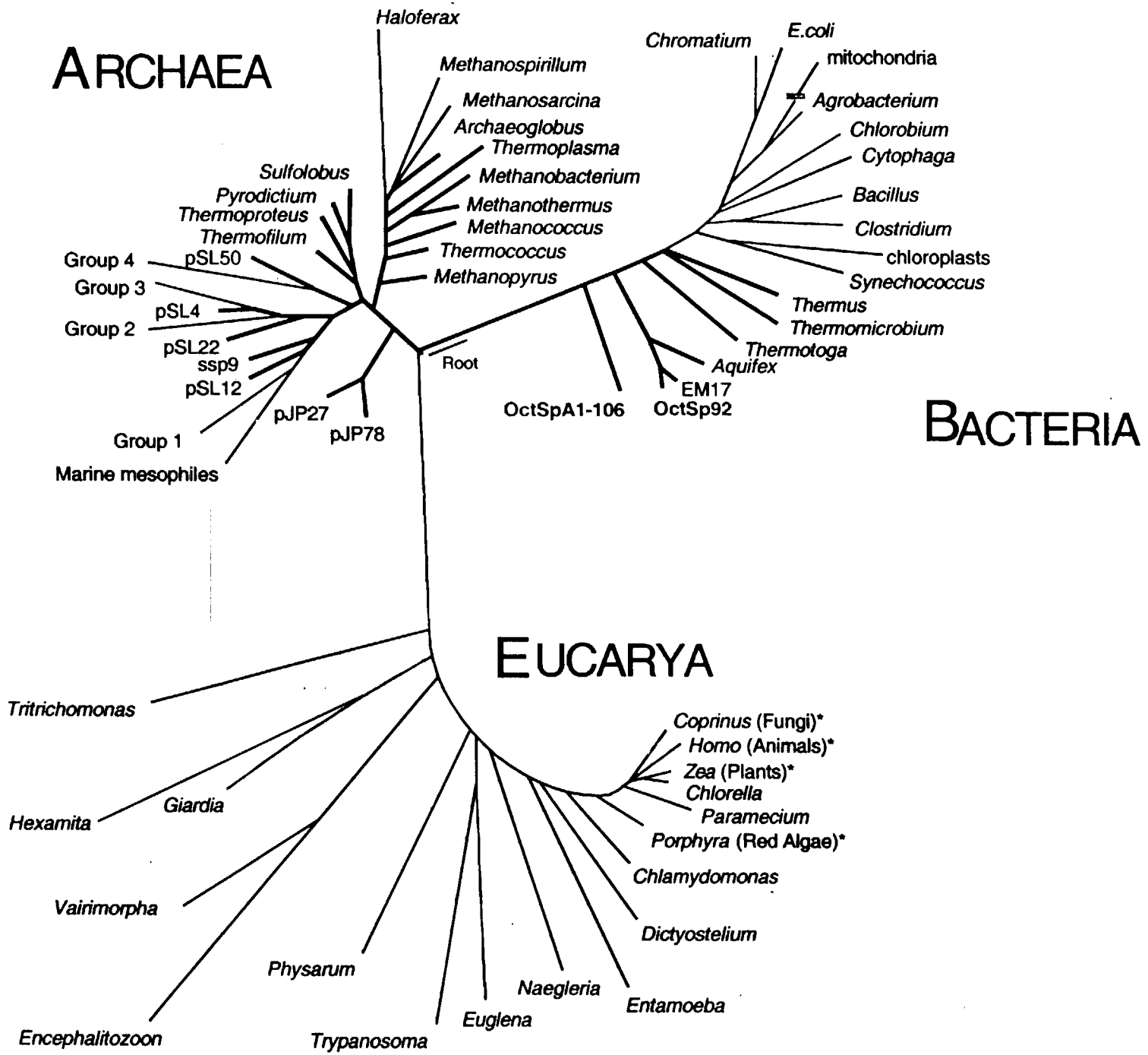
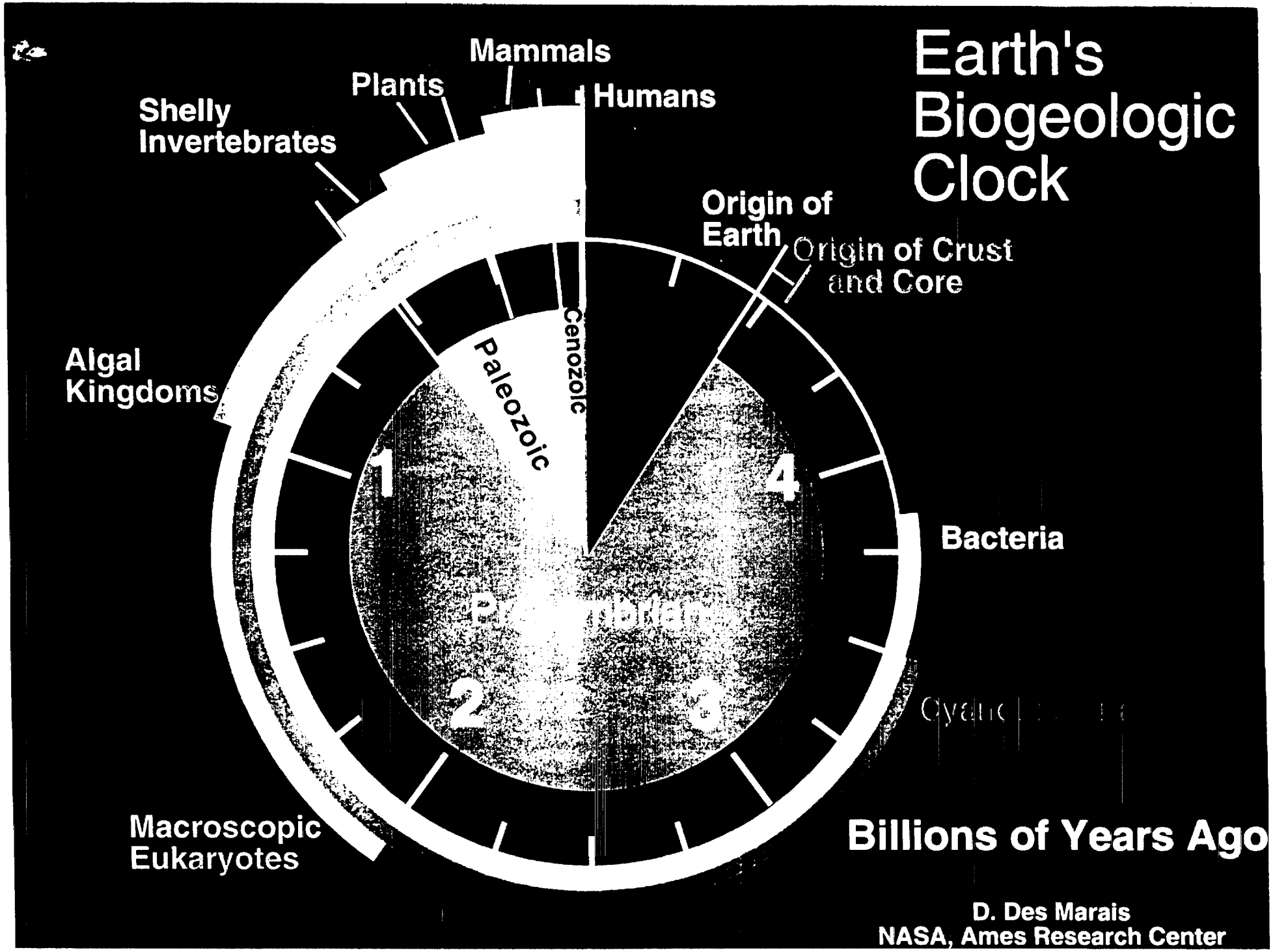

ARCHAEA
Haloferax
Methanospirillum
Methanosarcina
Archaeoglobus
Thermoplasma
Methanobacterium
Methanothermus
Methanococcus
Thermococcus
Methanopyrus
Sulfolobus
Pyrodictium
Thermoproteus
Thermofilum
pSL50
Group 4
Group 3
pSL4
Group 2
pSL22
ssp9
pSL12
Group 1
Marine mesophiles
pJP27
pJP78
Root
Chromatium
E.coli
mitochondria
Agrobacterium
Chlorobium
Cytophaga
Bacillus
Clostridium
chloroplasts
Synechococcus
Thermus
Thermomicrobium
Thermotoga
Aquifex
EM17
OctSp92
OctSpA1-106
BACTERIA
EUCARYA
Tritrichomonas
Hexamita
Giardia
Vairimorpha
Encephalitozoon
Physarum
Trypanosoma
Euglena
Naegleria
Entamoeba
Dictyostelium
Chlamydomonas
Porphyra (Red Algae)*
Paramecium
Chlorella
Zea (Plants)*
Homo (Animals)*
Coprinus (Fungi)*


Earth's Biogeologic Clock
Mammals
Plants
Humans
Shelly Invertebrates
Origin of Earth
Origin of Crust and Core
Algal Kingdoms
Cenozoic
Paleozoic
1
4
2
3
Bacteria
Macroscopic Eukaryotes
Billions of Years Ago
D. Des Marais
NASA, Ames Research Center